Inorganic Triphenylphosphine

Adam D. Gorman, Jonathan A. Bailey, Natalie Fey, Tom A. Young, Hazel A. Sparkes, Paul G. Pringle*

Abstract: A completely inorganic version of one of the most famous organophosphorus compounds, triphenylphosphine, has been prepared. A comparison of the crystal structures of inorganic triphenylphosphine, $PBaz_3$ (where Baz = $B_3H_2N_3H_3$) and PPh_3 shows that they have superficial similarities and furthermore, the Lewis basicities of the two compounds are remarkably similar. However, their oxygenation and hydrolysis reactions are starkly different. $PBaz_3$ reacts quantitatively with water to give PH_3 and with the oxidizing agent $ONMe_3$ to give the triply-O-inserted product $P(OBaz)_3$, an inorganic version of triphenylphosphite; a corresponding transformation with PPh_3 is inconceivable. Thermodynamically, what drives these striking differences in the chemistry of $PBaz_3$ and PPh_3 is the great strength of the B–O bond.

The diatomic fragments BN and CC are isoelectronic and the chemical consequences of this simple relationship have been appreciated ever since the 1926 discovery of borazine which is isoelectronic to benzene and dubbed "inorganic benzene" (Figure 1).[1] The substitution of a BN unit for a CC in an organic molecule has a transformative effect on the properties of the compound as illustrated by the three comparisons given in Figure 1 from the fields of photochemistry,[2–7] medicinal chemistry[8–13] and hydrogen storage.[14–18]

Since BN and CC are considered to be isosteres, the explanation for the sharply different properties of BN / CC analogues most likely lies in differences in the bonding and electronegativity. The energies and sizes of the atomic orbitals formally combining to form the molecular orbitals of a CC bond are self-evidently matched whereas the mismatched energies and sizes of the atomic orbitals combining in the BN bond make the σ-bonding dipolar and the π-bonding weaker due to less efficient overlap.[19–22] The result is that BN compounds are generally kinetically and thermodynamically more reactive than their CC analogues. Thus, borazine has superficial similarities with benzene (e.g. both are colourless liquids under ambient conditions) but the aromaticity of borazine, as determined computationally and experimentally, is significantly lower than the aromaticity of benzene (e.g NICS values for benzene and borazine are -11.5 and -2.1 respectively),[23–25] and the dominant mechanisms by which they undergo substitution are fundamentally different: electrophilic aromatic substitution for benzene, addition-elimination for borazine.[26,27]

B-trisubstituted borazines (Figure 2) are readily prepared and their chemistry has been well studied[28–33] but the chemistry of the less accessible B-monosubstituted borazines (XBaz, Figure 2) has been little developed;[34–36] for example, 2-hydroxyborazine (HOBaz), the borazine analogue of phenol, has only been partially characterised *in situ* as part of a mixture of products formed in the photochemical oxidation of borazine.[37] In addition, no borazines that contain P–B bonds have been reported which may be due to the anticipated high reactivity of the P–B bond.[38]

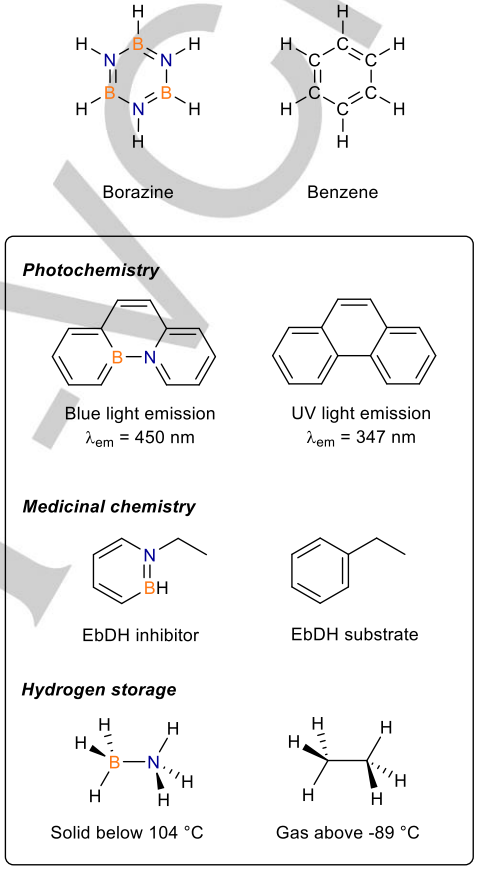

Figure 1. Examples of isoelectronic compounds featuring BN for CC substitution.

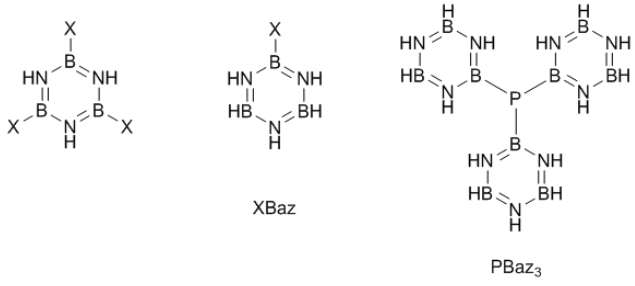

Figure 2. Examples of substituted borazines.

There are thousands of academic articles and patents featuring PPh_3 and globally it is produced on a multi-kiloton scale per annum because of its multitude of applications.[39,40] We were intrigued to know whether it would be possible to make "inorganic" triphenylphosphine (Figure 2, tris(2-borazinyl)phosphine; $PBaz_3$) and if so, how its properties would compare with "conventional" triphenylphosphine (PPh_3). Here we report the successful synthesis of $PBaz_3$ and show that it has

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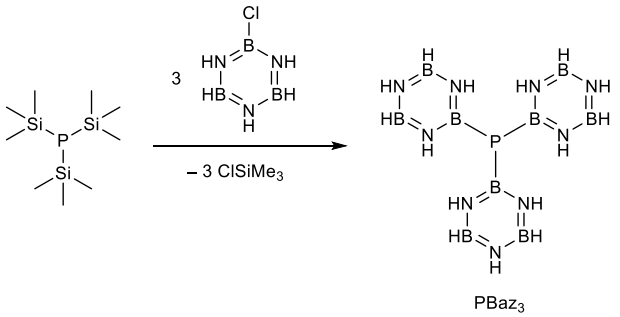
Lewis basicity similar to that of PPh_3 but the high reactivity of the P–B bond leads to oxygenation chemistry that is unprecedented with conventional phosphines.

Synthesis and characterization of $PBaz_3$. We have previously shown that P–B bonds can be readily formed by a chlorosilane elimination reaction between a chloroborane and a silylphosphine.[41] Pleasingly, the reaction between chloroborazine and $P(SiMe_3)_3$ produced $PBaz_3$ quantitatively (Scheme 1) according to multinuclear NMR spectroscopy (see Supporting Information for details). The reaction was monitored by ^{31}P NMR spectroscopy which showed that the conversion of $P(SiMe_3)_3$ to $PBaz_3$ proceeded smoothly over 5 h via two intermediates which are assigned to the monoborazinyl $(Me_3Si)_2PBaz$ and diborazinyl $Me_3SiPBaz_2$.



Scheme 1. Synthesis of tris(2-borazinyl)phosphine ($PBaz_3$).

The white, malodorous, solid $PBaz_3$ was isolated in yields of up to 97% simply by removal of the volatiles. The ^{31}P NMR spectrum of solutions of $PBaz_3$ in THF under argon at ambient temperatures is unchanged over a period of one month. The ^{31}P NMR signal at -205 ppm for $PBaz_3$ is very broad ($w_{1/2}$ = 340 Hz) and remains broad at high (+80 ˚C) temperatures, consistent with short quadrupolar relaxation times and unresolved coupling to the nine $^{11}B/^{10}B$ nuclei. The δ_P of $PBaz_3$ is 200 ppm to high field of PPh_3 (δ_P = -5.0 ppm), and much closer to that of $P(SiMe_3)_3$ (δ_P = -251 ppm) and PH_3 (δ_P = -241 ppm) reflecting the very different magnetic environments of the P atom in $PBaz_3$ and PPh_3. The ^{11}B and ^{1}H NMR spectra of $PBaz_3$ show the expected signals.

Crystals of $PBaz_3$ suitable for X-ray crystallography were obtained from its saturated solution in CH_2Cl_2 stored at -20 °C and its crystal structure is shown in Figure 3 alongside the structure of PPh_3.[42] The molecular structure of $PBaz_3$ shows a propeller-like orientation of the planar borazinyl substituents with near C_3 symmetry and a pyramidal geometry at phosphorus. Ostensibly the structures of $PBaz_3$ and PPh_3 are similar but they differ significantly in the details: (1) The P–B bond lengths in $PBaz_3$ are *ca.* 0.1 Å longer than the P–C bond lengths in PPh_3 paralleling the difference in the covalent radii (r_C = 0.73(2) Å, r_B = 0.84(3) Å). (2) The geometry at P in $PBaz_3$ is considerably flattened, in accord with Bent's Rule[43] which predicts that the p-character of P–X π-bonds (e.g. in PX_3 where X = F, OR, NR_2, CR_3, BR_2) should decrease with decreasing electronegativity of X; the flattening at P is also consistent with some π-character in the P–B bonds (see below). (3) The orientation of the rings in $PBaz_3$ is less propeller-like than in PPh_3 as is clear by comparison of the side-on views in Figure 3 which show that the acute angle (56˚) between the planes of the rings in $PBaz_3$ contrasts with the approximately orthogonal (82˚) rings in PPh_3. (4) The long P–B bonds make the P atom less crowded in $PBaz_3$ than in PPh_3 as shown by the calculated crystallographic cone angles[44] of 137˚ ($PBaz_3$) and 154˚ (PPh_3).

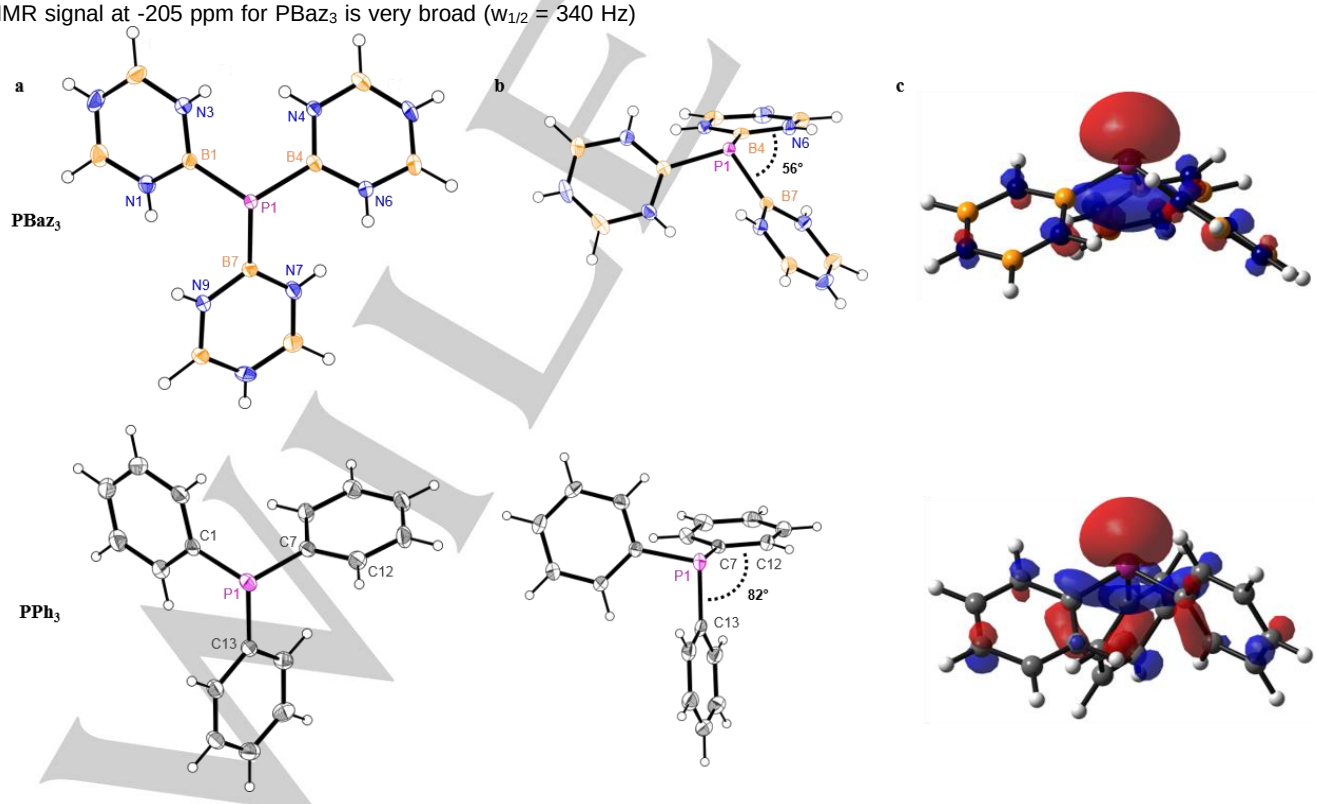
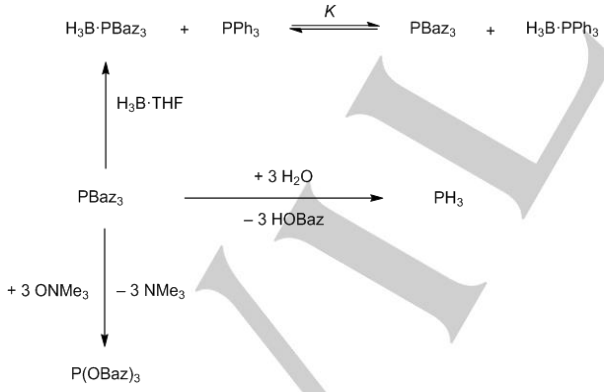


Figure 3. Molecular structures of $PBaz_3$ and PPh_3.[42] Two views of the structures are given: (a) along the C_3 axis and (b) perpendicular to the C_3 axis, to facilitate the comparison. (c) Plots of the HOMOs of $PBaz_3$ and PPh_3 (isovalues 0.05). Selected bond lengths (Å) and angles: P1-B1 1.923(2), P1-B4 1.9230(19), P1-B7 1.9255(18), B1-P1-B4 106.34(8), B4-P1-B7 107.78(8), B1-P1-B7 107.44(8), B1-P1-B7-N9 52.94(11), B7-P1-B4-N6 55.98(10), B4-P1-B1-N3 57.74(10).

DFT calculations have been carried out (PBE0-D3BJ/cc-pVTZ) in order to compare the electronic structures of $PBaz_3$ with PPh_3. Both calculated structures closely matched the structures obtained by X-ray crystallography (see SI). The surface contour maps of the canonical HOMOs for $PBaz_3$ and PPh_3 are clearly identifiable as the lone pairs on the P atoms (Figure 3c) and the calculated energies of these orbitals are very similar: -6.165 eV (PPh_3) and -6.321 eV ($PBaz_3$). NBO calculations show that the HOMO of $PBaz_3$ has 64% p-character which is significantly more than the 54% for PPh_3; the greater p-character is also apparent from the shapes of the HOMO orbitals (Figure 3c). The calculated bond indices for P–B in $PBaz_3$ (1.07) and P–C in PPh_3 (0.92) support the idea that there is a small amount of P–B π-bonding present in $PBaz_3$.[45]

Reaction of $PBaz_3$ with BH_3. Addition of $H_3B{\cdot}THF$ to $PBaz_3$ generated a product that has been characterised in solution by ^{31}P and ^{11}B NMR spectroscopy and assigned the structure $Baz_3P{\cdot}BH_3$ (Scheme 2); the analogous $Ph_3P{\cdot}BH_3$ is formed similarly from $H_3B{\cdot}THF$ and PPh_3.[46] The ^{31}P and ^{11}B NMR signals for the $Baz_3P{\cdot}BH_3$ are at δ_P = -171 and δ_B = -42 ppm which correspond to coordination chemical shifts of $\Delta\delta_P$ = +34 and $\Delta\delta_B$ = -41 ppm; these values are similar to those for $Ph_3P{\cdot}BH_3$ ($\Delta\delta_P$ = +26 and $\Delta\delta_B$ = -38 ppm).

In order to determine the relative Lewis base strengths of $PBaz_3$ and PPh_3, the position of the equilibrium shown in Scheme 2 has been investigated by ^{31}P NMR spectroscopy. When $Ph_3P{\cdot}BH_3$ and $PBaz_3$ or $Baz_3P{\cdot}BH_3$ and PPh_3 were mixed in THF, an equilibrium was slowly established over several hours in favour of $Ph_3P{\cdot}BH_3$ and integration of the ^{31}P NMR signals for the constituents led to an estimate of the equilibrium constant *K* to be ~140. Since this equates to a ΔG ~ 3 kcal mol^{-1}, it is concluded that the Lewis basicity of PPh_3 is similar but slightly greater than $PBaz_3$. Our calculations (DLPNO-CCSD(T)/def2-TZPP//PBE0-D3BJ/def2-SVP) show that the borane binding enthalpy (calculated *in vacuo* and neglecting entropic corrections) of PPh_3 (34 kcal mol^{-1}) is greater than that of $PBaz_3$ (26 kcal mol^{-1}) in line with the experimental observation favoring $PPh_3.BH_3$.

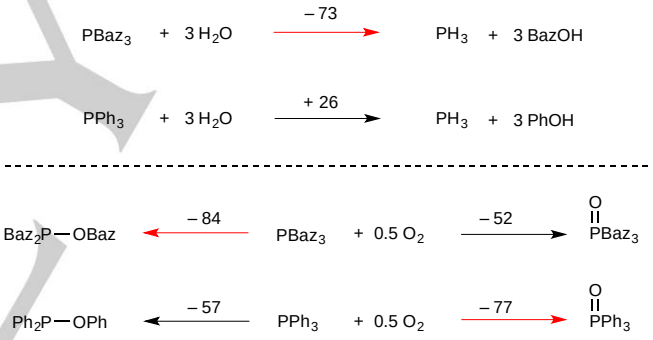


Scheme 2. Reactions of $PBaz_3$ with BH_3, H_2O and $ONMe_3$.

Hydrolysis and oxygenation of $PBaz_3$. The reactivity of the P–B bond in $PBaz_3$ towards water and oxidizing agents is very different from the P–C bond in PPh_3. For example, while PPh_3 is completely inert to water, $PBaz_3$ is extremely moisture sensitive. $PBaz_3$ reacts rapidly and quantitatively with water to give PH_3 (δ_P = -241 ppm, quartet, J_{PH} = 187 Hz) and a species tentatively assigned to 2-hydroxyborazine (HOBaz, Scheme 2) on the basis of the ^{11}B NMR spectrum which showed a doublet at +30 ppm ($^1J_{BH}$ = 139 Hz) and a singlet at +24 ppm in a 2:1 intensity ratio.

When a sub-stoichiometric amount of H_2O was added to $PBaz_3$, the ^{31}P NMR spectrum of the resulting solution contained two species in addition to $PBaz_3$ and PH_3 and these are assigned, on the basis of their ^{31}P parameters, to the intermediate secondary phosphine Baz_2PH (δ_P = -203 ppm, doublet, J_{PH} = 200 Hz) and primary phosphine $BazPH_2$ (δ_P = -228 ppm, triplet, J_{PH} = 203 Hz) (see Supporting Information); the J_{PH} values for Ph_2PH (216 Hz) and $PhPH_2$ (199 Hz) are very similar to the borazinylphosphine analogues. The hydrolysis of $PBaz_3$ is reminiscent of the hydrolysis of $P(SiMe_3)_3$ under the same conditions to give $H_nP(SiMe_3)_{3-n}$ (n = 1-3; see Supporting Information for details); this is an illustration of the similar reactivity of P–B and P–Si bonds which can be viewed as a manifestation of the B/Si diagonal relationship.

The Gibbs free energy change (ΔG) for the observed $PBaz_3$ hydrolysis to PH_3 was calculated to be -73 kcal mol^{-1} (using our standard DLPNO-CCSD(T) approach) which is a strong thermodynamic driving force and almost 100 kcal mol^{-1} more favourable than the ΔG calculated for the analogous hypothetical PPh_3 hydrolysis (+26 kcal mol^{-1}, Scheme 3). This contrasting outcome is attributed to B–O bonds (~130 kcal mol^{-1}) being much stronger than C–O bonds (~85 kcal mol^{-1}).



Scheme 3. Thermodynamics of hydrolysis and oxygenation of PPh_3 and $PBaz_3$. Values of ΔG in kcal mol^{-1}; the red reaction arrows indicate the experimentally observed reactions.

We have previously shown that O atoms can be inserted into the P–B bonds of borylphosphines by treatment with $ONMe_3$; this occurred even when the P lone pair of the borylphosphine was coordinated to Rh.[47] It was therefore of interest to investigate whether inorganic triphenylphosphine, $PBaz_3$ could be converted directly to inorganic triphenylphosphite, $P(OBaz)_3$ (Scheme 2). The *in situ* $^{31}P\{^1H\}$ NMR spectrum of the $PBaz_3/ONMe_3$ reaction mixture showed, after 5 min, a sharp singlet at δ_P +119 ppm (*cf.* for $P(OPh)_3$, δ_P 129 ppm) as the only P-containing product; this is a change in ^{31}P NMR shift of over +300 ppm from the signal of $PBaz_3$. Consistent with the structure of $P(OBaz)_3$, the ^{11}B NMR spectrum displayed two broad signals at +31 ppm ($^1J_{BH}$ ~ 125 Hz) and +23 ppm in a 2:1 ratio.

Treatment of PPh_3 with $ONMe_3$ gives $O{=}PPh_3$ whereas no similar reaction occurred to give $O{=}PBaz_3$ and the only observed product was the phosphite $P(OBaz)_3$. In order to probe the source of this sharp difference in chemistry, calculations were carried out on two alternative monooxygenation reactions (with O_2) that produce phosphine oxide or phosphinite (Scheme 3).

These calculations predict that there would be a strong thermodynamic preference for phosphinite formation with $PBaz_3$ but phosphine oxide formation with PPh_3. Calculated bond dissociation energies indicate that the P–B in $PBaz_3$ (90 kcal mol^{-1}) is stronger than the P–C in PPh_3 (81 kcal mol^{-1}) and therefore the unconventional oxidation chemistry of $PBaz_3$ is driven by the high B–O bond strength.

The chemistry of borazine has intrigued chemists for over 90 years. The synthesis of triborazinylphosphine ($PBaz_3$), an inorganic analogue of triphenylphosphine (PPh_3), is a notable achievement because it is the most elaborate molecular borazine so far reported and the first borazine to contain a B–P bond. The structures and Lewis basicity of $PBaz_3$ and PPh_3 are similar but their oxygenation and hydrolysis chemistry could hardly be more different. For example, $PBaz_3$ catches fire in air (presumably due to the formation of PH_3) while PPh_3 is indefinitely air-stable even in solution. Controlled oxidation transforms $PBaz_3$ into "inorganic triphenyl phosphite", $P(OBaz)_3$ by three O insertions into the P–B bonds while PPh_3 produces simply triphenylphosphine oxide. These striking differences in chemistry are thermodynamically driven by the very high B–O bond strength. The extreme sensitivity of $PBaz_3$ to air and moisture producing PH_3, precludes many applications for $PBaz_3$ in catalysis but its synthesis opens up the possibility of developing more stable ligands containing a single borazinyl substituent and the prospect of producing unchartered borazines that contain B bonded to other 2nd row elements such as Si and S.

Keywords: Main Group Elements • Phosphorus • Boron • Inorganic Chemistry • Structure Elucidation

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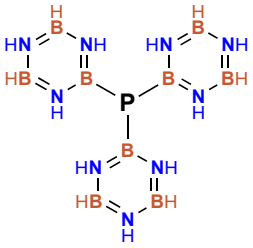
COMMUNICATION

Inorganic versus organic: the molecular structures and Lewis basicities of triphenylphosphine and tris(2-borazinyl)phosphine appear similar but their hydrolysis and oxygenation chemistry could hardly be more contrasting.



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